

IV.A.2 Development of High-Temperature Membranes and Improved Cathode Catalysts

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Subcontractors:

High-Temperature Membrane:

Virginia Polytechnic Institute and State University, Blacksburg, VA

IONOMEM, Marlborough, CT

Pennsylvania State University, University Park, PA

Stanford Research Institute International, Menlo Park, CA

Princeton University, Princeton, NJ

Cathode Catalysts:

United Technologies Research Center (UTRC), East Hartford, CT

Northeastern University, Boston, MA

University of South Carolina, Columbia, SC

Case Western University, Cleveland, OH

Objectives

- Develop and demonstrate an advanced polymeric membrane able to operate at near ambient pressure (1-1.5 atm) in the temperature range of 120-150°C that is able to meet DOE 2005 targets for performance.
- Develop and demonstrate improved Pt cathode catalysts that will enable the reduction of Pt loading and meet DOE 2005 target performance¹.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- **Phase 1:** High-temperature membranes (HTMs) and improved Pt cathode catalysts were synthesized, characterized and compared with issued specifications. [Finished]
- **Phase 2:** Laboratory-scale catalyst-coated membranes (CCMs) will be fabricated, optimized and tested using the Phase 1 down-selected membranes and catalysts. [In progress]
- **Phase 3:** Full-size CCMs with the down-selected and optimized HTMs and catalysts will be fabricated and tested in 2 individual multi-cell stacks.

Accomplishments

This project was initiated in Q1 2002. During the period of Q1 2002-Q1 2004, all subcontractors worked on the synthesis and optimization of novel catalysts and HTM systems. At the end of Q1 2004, Phase 1 of the project ended with the down-selection of the best systems.

- The membranes of five subcontractors [IONOMEM, Virginia Tech, Stanford Research Institute (SRI), Princeton, and Penn State (PSU)] were ranked based on their conductivity, water uptake, performance and durability at and around the operational design point of 120°C and 50% relative humidity (RH).
- IONOMEM's PTA doped membrane with resistivity of $0.1 \Omega\text{-cm}^2$ at 120°C and 50% RH and fuel cell performance overcoming Nafion 112 was down-selected for catalyst-coated membrane (CCM) optimization.
- Virginia Tech showed promising results with their biphenyl sulfones (BPSH), but they performed worse than Nafion[®] 112. Virginia Tech was down-selected to work on further material development.
- A model for reversible potential for the formation of reaction intermediates on electrocatalyst surfaces was run at Case Western Reserve University (CWRU) and has shown that the Pt skin on platinum alloyed with Cr and Co forms absorbed hydroxyl at higher potential than on the Pt (111) electrode surface.
- The Pt alloys from three subcontractors [University of South Carolina (USC), Northeastern University (NEU) and United Technologies Corporation Fuel Cells (UTC FC)] were ranked based on their activity and stability, and the down-select process was conducted.
- Higher-activity and more stable Pt alloys were synthesized at UTC FC using the carbothermal technique. PtCo/C and PtIrCo/C catalysts were down-selected for catalyst-coated membrane optimization.
- NEU PtCo/C system synthesized using a colloidal sol-gel technique was down-selected for further work toward the improvement of material properties.
- CCM optimization process is in progress for IONOMEM's membrane and UTC FC's Pt alloy catalysts.

Introduction

Two main challenges in the proton exchange membrane (PEM) fuel cell area are the reduction of Pt loading and development of membranes that can operate at over 120°C. Overcoming these two challenges will directly impact the cost, performance and size of PEM fuel cell stacks. In order to achieve the aggressive DOE performance targets, new polymeric membranes with low thermal degradation and acceptable proton conduction at 120°C are needed. On the cathode catalyst part of the project, a combination of high-activity alloy catalysts can lead to thinner low-Pt-loading catalyst

layers and in such way reach the established performance and cost requirements.

Approach

To develop HTMs and novel cathode catalysts, UTC FC has teamed with research groups that possess competencies in the fields of polymer chemistry, electrocatalysis and engineering. The subcontractors that were participating in Phase 1 of the project together with the description of the approaches for membrane/catalyst synthesis are shown in Table 1 and Table 2.

Table 1. High-Temperature Membrane Project Participants (Phase 1)

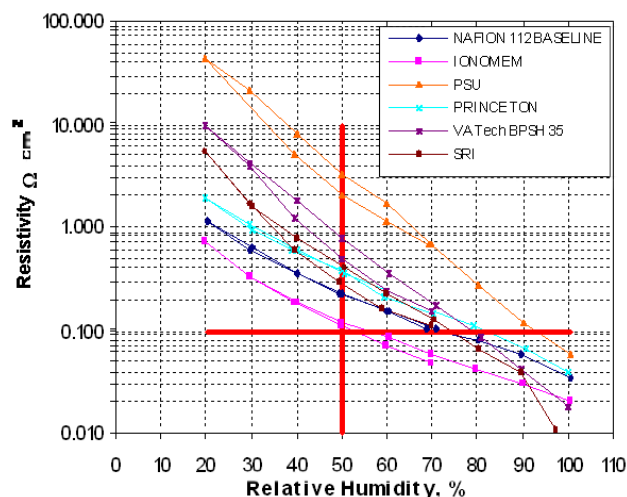
Group	Principal Investigator	Approach
IONOMEM	Mr. Leonard Bonville	Hygroscopic solid ion conductor (e.g., zirconium phosphate, etc.) filled Nafion®
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA; Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/ Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Table 2. Advanced Cathode Catalyst Project Participants (Phase 1)

Group	Principal Investigator	Approach
North Eastern University (NEU)	Prof. Sanjeev Mukerjee	Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys
University of South Carolina (USC)	Prof. Branko Popov	Pulse electro-deposition of Pt and Pt alloys on Carbon [Pt and Pt-X; X=Fe, Ni, Co, Mn and Cu]
UTC Fuel Cells (UTC FC)	Dr. Jeremy Meyers	Carbothermal synthesis of ternary Pt alloys [Pt-Ir-X and Pt-Rh-X [X =Ni, Co and V]]
Case Western Reserve University (CWRU)	Prof. Alfred Anderson	Quantum chemical modeling of Pt alloys and ORR
United Technologies Research Center (UTRC)	Dr. Ned Cipollini	Reproducible and stack-size CCM fabrication

Results

The project was initiated in Q1 2002. The first 2 years of the project were dedicated to material development, ex-situ screening and modeling work. UTC FC has stressed the importance of the

**Figure 1.** Comparison of the Area Specific Resistivities ($\Omega \text{ cm}^2$) of the Various Subcontractors' Membranes to Nafion®

conductivity requirements for HTMs at 120°C and 50% RH. Results were compared to Nafion® 112. Under Catalyst Development, commercial carbon-supported pure Pt was used as a baseline catalyst. Phase 1 was concluded in March 2004 by a down-selection process. Phase 2 is currently in progress. The majority of the work in this phase is dedicated to CCM optimization and durability studies of the down-selected materials. In addition, two subcontractors, whose materials showed promising results but performed below established baselines, were selected to further work on material properties improvement. These subcontractors (Virginia Tech on HTM and NEU on catalyst projects) will be required to submit their materials for final testing in the end of 2004.

Phase 1. Down-Select Results

High-Temperature Membrane: Five different membranes were subjected to ex-situ tests that included conductivity, water uptake, mechanical/ structural strength, and dimensional changes. All the measurements were conducted under elevated temperature at low humidity, or after the membranes were subjected to these conditions for a set period of time. The emphasis was set on conductivity values. Figure 1 shows the area specific resistivities of the various membranes as calculated from the thickness and the 4-electrode conductivity measurements.

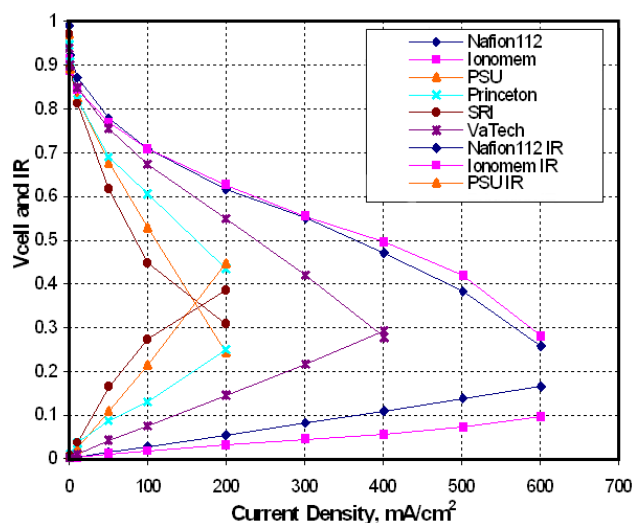


Figure 2. Comparison of the Performance of the Various Subcontractors' Membranes to Nafion®; 120°C, BOL, 50% RH, 150 kPa (abs), U: 30% / 25%

The target data point for the study is 120°C, 50% RH. At this point, only IONOMEM approached the cut-off target imposed in the project. No other membrane, including the Nafion® baseline, reached this resistivity target except at RH values exceeding 70%.

All the membranes were also tested in fuel cells at 120°C and 50% RH for performance and stability. Figure 2 shows the initial performance of the various subcontractors' membranes at 120°C and 50% RH. Under these conditions, the inlet oxygen concentration at 150 kPa was roughly 10.5%. Results clearly show that IONOMEM's performance is significantly greater than that of the other subcontractors under these conditions. In all cases, performance differences in the membranes are predominantly due to the difference in membrane conductivity. At UTC FC, each membrane was dry-pressed at 130°C between two catalyzed Toray gas diffusion layers (GDLs). The electrodes contained Nafion® ionomer and a catalyst loading of 0.4 mg Pt/cm² on the anode and cathode. The unitized electrode assemblies were then conditioned at 80°C and 75% RH before raising the operating temperature to 120°C, 50% RH.

The membranes were ranked based on results of tests (see Table 3), and the two best membranes were

Table 3. Results of the Down-Select Tests in HTM Program

Criteria	Criteria Subcategory	Weight	Ranking (1 to 5, 5 = highest, 0 = failure)					
			Nafion®	Ionomem	Va Tech	Princeton	SRI	PSU
Conductivity – 50 % Total	20% RH*	0.125	3	4	1	2	1	1
	50% RH*	0.25	3	4	2	2	2	1
Water Uptake – 20% Total	100% RH*	0.125	3	3	4	3	4	3
	40 % RH Vapor	0.15	3	3	1	2	2	2
	Liquid	0.05	3	2	5	1	1	1
Performance – 30% Total	IR BOL	0.1	3	4	3	2	1	2
	IR EOL	0.1	3	4	3	1	0	0
	crossover EOL	0.1	3	1	3	3	0	0
SCORE = $\sum(\text{Weight} * \text{Ranking})$			3.0	3.325	2.425	2.075	1.575	1.3

selected for Phase 2 of the project. IONOMEM's membrane was selected for CCM optimization and Virginia Tech was chosen to work on further membrane properties improvement.

Cathode Catalysts: Four catalyst systems from three subcontractors including USC, NEU and UTC FC were subjected to liquid cell tests and fuel cell performance measurements as a part of down-select process. Ex-situ electrochemical areas (ECAs) and oxygen redox reaction (ORR) activities, measured using rotating disk electrode (RDE) and fuel cell performance testing, were used for screening. Results of ex-situ measurements are shown in Table 4.

Table 4. Electrochemical Area and ORR Activities of Pt Alloy Cathode Catalysts

Catalyst	ECA, m ² /g	ORR activity, 0.9 V vs. RHE	
		μA/cm ²	A/g Pt
TKK-Pt/C	107.0	90	96
UTC-PtCo/C	74.0	274	203
UTC-PtIrCo/C	110.6	166	184
USC-PtCo/C	29.6	231	68
NEU PtCo/C	40.2	300	120

UTC FC catalyst systems have shown mass activity more than twice that of pure Pt catalyst. PtCo that was synthesized at NEU using a micellar

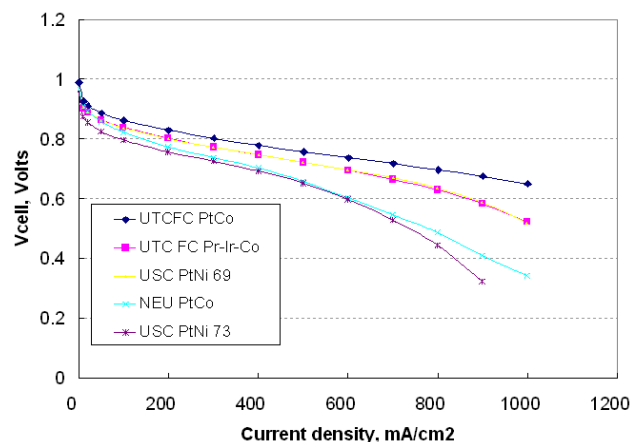


Figure 3. Results of Fuel Cell Performance Tests on Pt Alloy Cathode Catalysts (Testing conditions: H_2/Air , 65°C , 1 atm. Anode: Pt/C.)

technique has also shown activity higher than the Pt baseline.

All the catalyst systems were also tested in fuel cells as cathodes in CCMs. The state-of-the-art membrane electrode assemblies (MEAs) were fabricated at United Technologies Research Center (UTRC) using a screen-printing method. This fabrication method was tested prior to down-select. It has been shown earlier that UTRC MEAs are comparable to the commercial MEAs, and the performance reproducibility was shown to be excellent.² Results of fuel cell performance tests are shown in Figure 3.

In agreement with the RDE experiments, PtCo/C and PtIrCo systems synthesized at UTC FC using the carbothermal method showed superior performance and were down-selected for CCM optimization in Phase 2. NEU was selected to work on further improvement of their PtCo/C catalyst. Catalyst from USC showed high initial performance but rapidly decayed under fuel cell operating conditions.

In addition to the experimental work, extensive modeling effort was put into understanding Pt alloy behavior as catalysts for ORR. CWRU used a model for reversible potential for the formation of reaction intermediates on electrocatalyst surfaces. It was shown that the Pt skin on platinum alloyed with chromium or cobalt forms adsorbed hydroxyl at higher potential than on the Pt(111) electrode

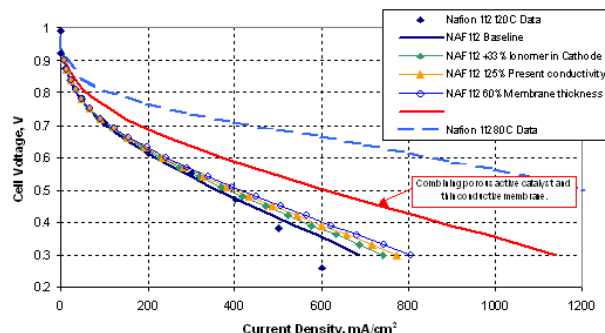


Figure 4. Simulation of Nafion® 112 Cell Performance at 120°C , 0 hours, 50% RH, 150 kPa (abs), s based on Bekktech data (Utilizations not taken into account)

surface. A correlation is found where the greater the amount of cobalt in the alloy, the greater the increase in the reversible potential. These results correlate with the decrease in overpotential for the four-electron reduction of oxygen that is observed on alloy cathodes relative to non-alloyed Pt electrodes, confirming that $\text{OH}(\text{ads})$ is a surface site blocker, causing the overpotential for oxygen reduction. Additional modeling work shows that in the first reduction step, $\text{OOH}(\text{ads})$ dissociates easily, forming $\text{O}(\text{ads})$ and $\text{OH}(\text{ads})$, and the adsorbed oxygen is reduced at a potential that is higher than that for $\text{OH}(\text{ads})$ reduction, which means that on Pt and the Pt skin, $\text{OH}(\text{ads})$ is the only surface poisoning intermediate, aside from $\text{H}_2\text{O}(\text{ads})$.

Phase 2. CCM Optimization

High-Temperature Membrane: The purpose of this phase is to optimize the CCM build of the down-selected membrane for performance and durability. UTC FC works hand-in-hand with IONOMEM/ University of Connecticut to address the issues of optimization. Several approaches are currently being examined, with priority on optimization of the ionomer content, catalyst and porosity of the cathode. A modeling effort is put into the understanding of the trends of the impact that various CCM changes can have on cell performance (see Figure 4).

Aspects of durability are being investigated, including Pt vs. Pt alloy dissolution at elevated temperatures and under cycling conditions, peroxide attack on the membrane, carbon corrosion and

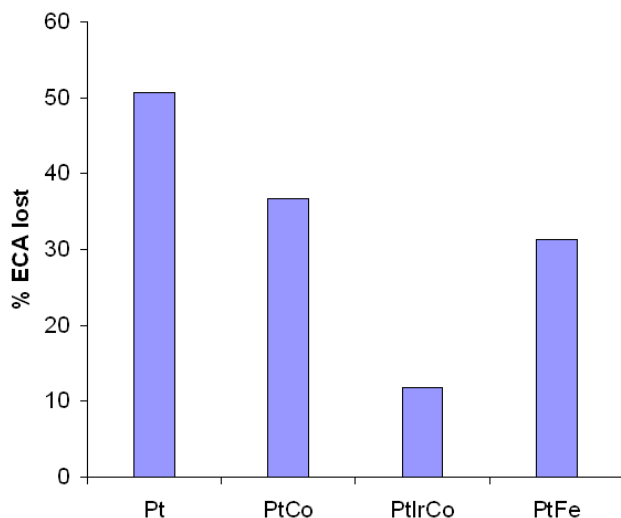


Figure 5. ECA Loss During Cyclic Durability Test

possible electrode structural changes. At present, several chemical stability and performance tests have been run, and preliminary data showed an increase in membrane degradation at 120°C and 50% RH. Two sources of performance degradation are being considered, namely electrode degradation losses and membrane decay losses.

Chemical stability tests (120°C, 50% RH, open circuit voltage) were performed on the down-selected membrane and have shown that the Teflon[®] backbone plays a beneficial role in arresting peroxide attack on the membrane. IONOMEM's PTA doped reinforced membrane survived the stability test for 36 hours. The Nafion[®] 112 baseline cell failed at 12 hours. Post-test EMPA analysis showed that membrane decay took place mainly on the anode side and was stopped/slowed down at the Teflon[®] backbone site. Clearly, before these membranes can be incorporated into fuel cell stacks, more work is needed to understand and mitigate failure modes under dry and high-temperature conditions.

Cathode Catalyst: For the development of Pt alloy systems, UTC FC has leveraged its past experience with the carbothermal technique for synthesis of Pt alloy/C catalysts. The carbothermal synthesis process involves precipitation of metal salts onto preplatinized carbon and heat treatment to form alloys.³ The carbon support during the heat treatment also serves as the reducing agent. To achieve combined activation and mass transport benefits, UTC FC has adopted a strategy to develop

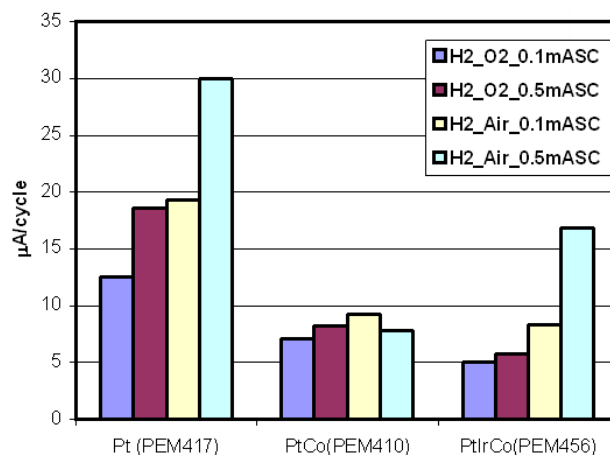


Figure 6. Average Decay Rate During Potential Cycling Test

higher activity and concentration (40-50 wt%) Pt alloy catalyst systems. The intent is to reduce the thickness of the catalyst layer, to facilitate mass transport within a catalyst layer, and to improve the cell power density at a high current density.

Because of different surface polarity of new Pt alloy catalysts, the CCMs have to be optimized. In particular, this concerns the optimization of ionomer content in the catalyst layer. Another aspect of MEA optimization that is currently being looked at by UTC FC is the use of alternative gas diffusion medias in order to improve mass transport of oxidant to reaction sites. At the same time, Pt loading is being reduced in the electrodes in order to achieve the aggressive 2005 goals set by DOE of 0.6 g_{Pt}/kW total loading.⁴

It has been shown previously that PtCo/C shows superior stability under fuel cell conditions compared to pure Pt catalyst. Cyclic durability studies carried out at UTC FC on PtIrCo/C showed that its durability is even better than the PtCo/C system. A fuel cell with PtIrCo/C used as cathode catalyst was subjected to potential cycling in the range of high voltages where Pt dissolution is expected to take place. Measurements of electrochemical area (ECA) show that only 10% of active area has been lost during the time of the experiment, and performance decay rates were much lower than that of pure Pt (see Figure 5 and Figure 6). Electron microprobe scans of the MEA were taken as part of post-test analysis and showed no Co or Ir migration into the membrane.

The absence of Co and Ir migration is a strong benefit for the PtIrCo/C system.

References

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2. FY 2003 Annual Report to DOE, Development of HTMs and Improved Cathode Catalysts
3. US Patents 5,013,618 and 4,447,506.
4. DOE Technical Targets Tables, Table 3.3.2, Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.